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Mixed oxides with layer lattices

III. Structure of $BaBi_4Ti_4O_{15}$

By BENGT AURIVILLIUS

With 4 figures in the text

X ray studies on the compounds $CaBi_2Nb_2O_9$ (1) and $Bi_4Ti_3O_{12}$ (2) have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from $Bi_2O_2^{2+}$ layers and perowskite layers. The unit cells are pictured schematically in Figs. 1 a and 1 c. It was found both for $CaBi_2Nb_2O_9$ and $Bi_4Ti_3O_{12}$ that the symmetry was body-centered pseudo-tetragonal and that the length of the a axes had the same value (3.8 Å) while the length of the c-axis was 25 Å for $CaBi_2Nb_2O_9$ and 33 Å for $Bi_4Ti_3O_{12}$. In both structures the heavy atoms form approximately a "substructure" with a smaller body-centered tetragonal cell with $a = 3.8$ Å and $c = 25/5$ Å for $CaBi_2Nb_2O_9$ or $c = 33/7$ Å for $Bi_4Ti_3O_{12}$.

The Bi_2O_2 layers and perowskite layers lie perpendicular to the c-axis. Similar layer structures have been found for a number of bismuth oxicompounds (3,4,5). The common structural element in all these compounds is quadratic Bi_2O_2 layers between which halides or certain radicals are inserted. This explains the fact that the a axes of all these compounds are of about the same length. For a survey see (5).

For the $CaBi_2Nb_2O_9$ type each perowskite layer has the composition $(CaNb_2O_7)_n$ and the height of the layer is equal to four distances Nb—O or approximately to the height of two $E2_1$ (perowskite) unit cells (see Fig. 1 a). A compound with a somewhat similar structure has previously been investigated by LAGERCRANTZ and SILLÉN (5). In this structure (see Fig. 1 b), beyerite $CaBi_2O_2(CO_3)_2$, the point positions corresponding to the positions of the Nb atoms in $CaBi_2Nb_2O_9$ are occupied by "rotating" CO_3^{2-} groups.

For the $Bi_4Ti_3O_{12}$ type the perowskite layers have the composition $(Bi_2Ti_3O_{10})_n$ and the height of the layer is equal to six distances Ti—O or approximately to the height of three $E2_1$ unit cells.

The general formula for a compound built up in a way similar to $CaBi_2Nb_2O_9$ but where the height of the perowskite layer enclosed between a pair of Me_2O_2 layers is equal to the height of m $E2_1$ cells, will be:

$$Me_2O_2\,(Me'_{m-1}\,R_m\,O_{3m+1}).\quad Me, Me': Ca, Sr, Ba\ Bi\ (K + Bi)/2\ etc.$$

$$R: Ti, Nb, Ta\ (Nb + Ti)/2\ etc.$$

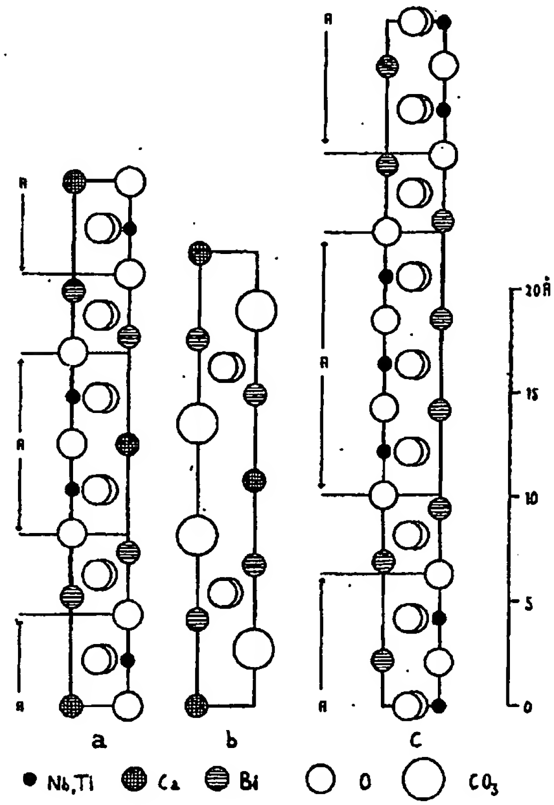
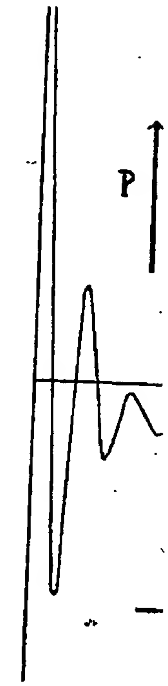


Fig. 1. Schematical pictures of the structures af a. $CaBi_2Nb_2O_9$ b. $CaBi_2O_2(CO_3)_2$ and c. $Bi_4Ti_3O_{12}$. The vertical lines indicate the lines $0\,0\,z$ and $\frac{1}{2}\,\frac{1}{2}\,z$ in the unit cells. A denotes perowskitic ($E2_1$) regions in the structures.

It seemed of interest to investigate whether compounds could be synthesized with $m = 4$. The present investigation shows that structures of the above type with $m = 4$ exist.

Mixtures of Bi_2O_3, $BaCO_3$ and TiO_2, corresponding to the composition $BaBi_4Ti_4O_{15}$ were prepared and heated to 1100° C. Single crystals, thin plates, were picked out and Weissenberg photographs were taken. These could be interpreted by means of a body-centered tetragonal cell with $a = 3.86$ Å and $c = 41.7$ Å. The strong lines of the powder photographs (taken from preparations heated to 900° C (Au crucible) or 1100° C (Pt crucible) were easily identified since they could all be described with the aid of the "sub-lattice" ($a =$ 3.86 $c = 41.7/9$). If the c axis were 9 fold even the weak lines could be explained (Table 3). In this way the cell edges were found to be $a = 3.864$ Å and $c = 41.76$ Å. The observed density was 7.2, which agrees fairly well with the assumption of 2 formula units/unit cell (calculated density 7.49).

The Weissenberg photographs registered $0kl$, $1kl$, hhl and $h, h+1, l$. In the Weissenberg and powder photographs there was nothing to indicate a lower Laue symmetry than $D_{4h}-4/mmm$. Except for the extinctions due to the body-centering, hkl occurring only for $h + k + l = 2n$, no systematic extinctions were found, which is characteristic of the space groups C_{4v}^{9}, $D_{2d}^{9,11}$ and D_{4h}^{17}. Fig. 2



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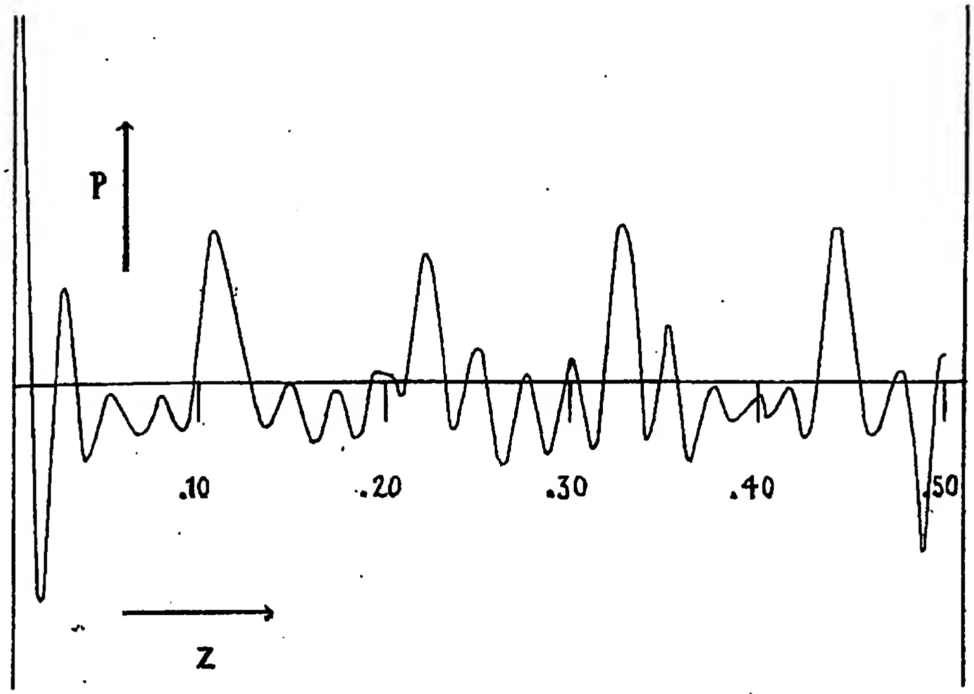

Fig. 2. Patterson Harker function of $BaBi_4Ti_4O_{15}$ along 0 0 z. All observed reflexions were used for this calculation.

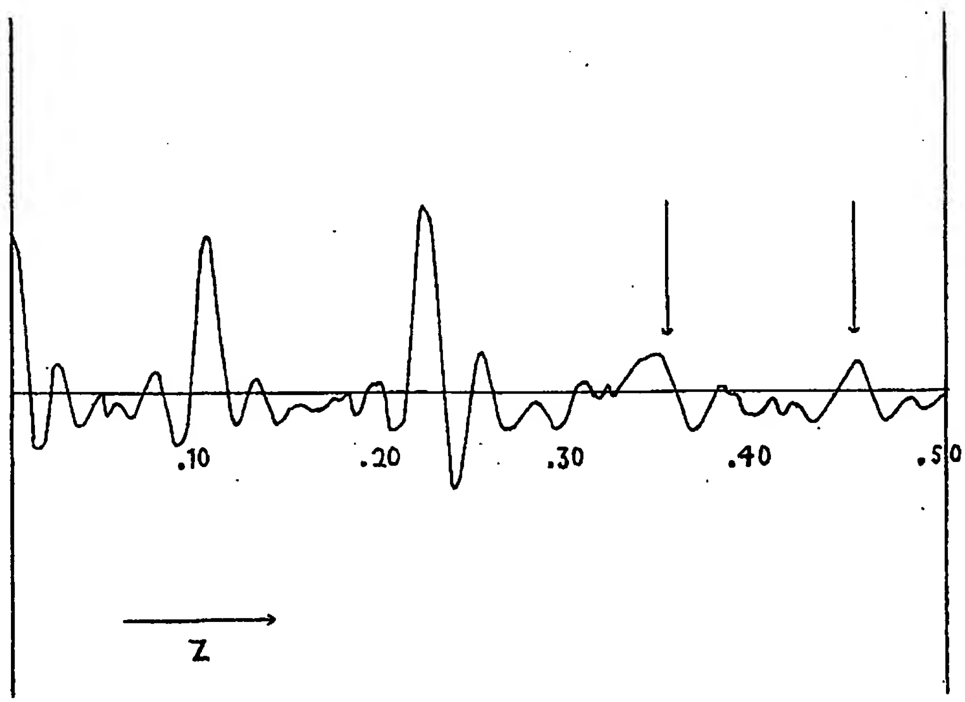

Fig. 3. Three dimensional Fourier cut along 0 0 z for $BaBi_4Ti_4O_{15}$. The same intensity material was used as for the Patterson Harker analysis pictured in Fig. 2. The signs of the amplitudes are the same as those obtained in the structure factor calculation for Table 2. The vertical arrows correspond to the z_{Ti} values actually assumed.

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shows the Patterson Harker function along $0\,0\,z$. For all observed reflexions the F^2 values were estimated from: $F^2 \approx I_{obs.} \dfrac{\sin 2\,\theta}{1 + \cos^2 2\,\theta}$. As expected large peaks appear at $z \approx 1/9$ $2/9$ $3/9$ and $4/9$.

It is interesting to compare the cell dimensions found above with the ones which might be expected if the compound $BaBi_4Ti_4O_{15}$ is assumed to have a structure similar to that of $CaBi_2Nb_2O_9$ but with $m = 4$. In this case the a axis would have about the same value as found. The length of the c axis might be estimated in the following way: The c axis of Bi_3NbTiO_9 ($m = 2$ see (1)) is 25.11 Å; the value for $Bi_4Ti_3O_{12}$ ($m = 3$ see (2)) is 32.83, the difference is 7.72. If twice this value is added to the c axis of $BaBi_2Nb_2O_9$ ($m = 2$) the value 41.0 Å is obtained. The value actually found was, as mentioned above, 41.76 Å.

From the composition, cell dimensions, and crystal symmetry it seemed *a priori* probable that the structure of $BaBi_4Ti_4O_{15}$ was the one we anticipated. Therefore, the parameters were worked out with the aid of the parameters found for

Table 1

Weissenberg photographs of $BaBi_4Ti_4O_{15}$. Cu K_α radiation. For zero order photographs the regions of maximum absorption (see Wells (6)) are indicated by dotted lines. The intensities of 1 0 1, 1 0 3 and 1 0 5 have been taken from a zero order photograph, those of 1 0 27—1 0 49 from a first order photograph rotated around (1 0 0).

l	0 0 1	2 0 1	2 2 1	4 0 1	1 1 1	3 1 1	3 3 1
2		—	vw	—	—	—	vw
4		—	—	—	vw	—	vvw
6	vw	vvw	vw	—	w	—	vvw
8	m	m	w	—	m	vvw	vvw
10	m	m	w	—	st	vw	w
12	w	vvw	vw	—	vvw	—	w
14	w	—	vvw	—	w	—	—
16	st	w	m^+	vvw	m	vvw	m
18	vst	m	st	w	vst	w	st
20	st	w	w	vvw	w	—	—
22	m^+	vvw	vvw	vvw	vw	—	vw
24	w	vvw	vvw	vvw	vw	—	w
26	w	vvw	—	—	w	vvw	w
28	st	m^+	w^+	m	m	vw	
30	w	w	w	m^+	—	vw	
32	w	w^+	w		m	w	
34	m	m	m^+		m	m	
36	st	st	st		m^+	m	
38	vvw	—	—		w	—	
40	st	st	st		st	st	
42	vvw	—			vw		
44	—	—			—		
46	m	m			st		
48	w	m			st		
50	w^+				m		
52	w^+						

Table 1 (cont.)

Weissenberg photographs of $BaBi_4Ti_4O_{15}$. Cu K_α radiation.

l	101	211	301	321	411
1	m	w	vw	vw	—
3	vvw	vvw	—	vvw	—
5	vvw	—	—	—	—
7	w	vw	vvw	w	—
9	vst	st	m	m	w
11	—	—	—	—	—
13	w	—	—	—	—
15	w$^+$	—	vvw	—	—
17	m	vvw	vvw	—	—
19	st	vw	vvw	vvw	vvw
21	w	—	vvw	vvw	vvw
23	w	—	vvw	vvw	m
25	m$^+$	vw	vw	vw	m$^+$
27	st	m	w	m	
29	m	vw	vvw	vvw	
31	m	w	vw	vw	
33	vw	vvw	vvw	vw	
35	—	—	—		
37	m$^+$	m	m		
39	vw	w	m		
41	w	w	w$^+$		
43	w$^+$	m			
45	m	m$^+$			
47	—				
49	st				
51	—				

Bi_3NbTiO_9 and $Bi_4Ti_3O_{12}$. The positions of the heavy atoms might be expected to be: 2 Ba in $0 0 0$, 4 Bi in $\pm 0 0 z_1$, 4 Bi in $\pm 0 0 z_2$.

The positions of the Ti and O atoms might be expected to be:

$$4 \text{ Ti in } \pm 0 0 z_3, \quad 4 \text{ Ti in } \pm 0 0 z_4, \quad 2 \text{ O in } 0 0 \tfrac{1}{2}, \quad 8 \text{ O in } \pm (0 \tfrac{1}{2} (\tfrac{1}{2} - z_3), \ \tfrac{1}{2} 0 (\tfrac{1}{2} - z_3)), \quad 8 \text{ O in } \pm (0 \tfrac{1}{2} (\tfrac{1}{2} - z_4), \ \tfrac{1}{2} 0 (\tfrac{1}{2} - z_4)), \quad 4 \text{ O in } \pm 0 0 (z_3 + z_4)/2$$

$$4 \text{ O in } \pm 0 0 (z_3 - (z_4 - z_3)/2), \quad 4 \text{ O in } 0 \tfrac{1}{2} \tfrac{1}{4}, \tfrac{1}{2} 0 \tfrac{1}{4}$$

$$z_1 \approx 1/9 \quad z_2 \approx 2/9 \quad z_3 \approx 0.350 \quad z_4 \approx 0.450$$

These atomic positions would give rise to high peaks in the Patterson-Harker plot at the same values as actually found. The calculated area ratios agree, however, with the observed ones only in as much as the biggest area is found for the peak at 1/9. The reasons might be an incorrect choice of the zero level and errors in the estimation of the intensities.

The parameters were varied around the above values for different positions of the Ba atoms: 2 Ba in $0 0 0$, $0 0 z_1$ or $0 0 z_2$, 2 Ba equally distributed over $(0 0 0 + 0 0 z_1)$, $(0 0 0 + 0 0 z_2)$, $(0 0 z_1 + 0 0 z_2)$ or $(0 0 0 + 0 0 z_1 + 0 0 z_2)$. The best agreement seemed to be for $z_1 = 0.106 \pm 0.001$, $z_2 = 0.221 \pm 0.001$, $z_3 = 0.352 \pm 0.004$, $z_4 = 0.452 \pm 0.004$ with 2 Ba equally distributed over $(0 0 0 + 0 0 z_1 +$

Table 2

Weissenberg photographs of $BaBi_4Ti_4O_{15}$. Cu K_α radiation

Icalc. = $(2.5\ F/f_{Bi})^2$

l	Iobs. 101	Icalc. 101	Iobs. 211	Icalc. 211	Iobs. 301	Icalc. 301
1	m	73	w	90	vw	94
3	vvw	5.8	vvw	7.3	—	8.4
5	vvw	4.8	—	5.8	—	5.8
7	w	30	vw	31	vvw	32
9	vst	620	st	610	m	630
11	—	13	—	12	—	14
13	w	25	—	24	—	24
15	w+	62	—	60	vvw	60
17	m	94	vvw	92	vvw	90
19	st	160	vw	170	vvw	170
21	w	15	—	12	vvw	12
23	w	19	—	18	vvw	18
25	m+	120	vw	120	vw	120
27	st	320	m	320	w	320
29	m	45	vw	45	vvw	44
31	m	160	w	160	vw	160
33	vw	56	vvw	56	vvw	56
35	—	13	—	12	—	12
37	m+	300	m	300	m	300
39	vw	12	w	13	m	13
41	w	15	w	14	w+	15
43	w+	200	m	200		
45	m	180	m+	180		
47	—	18				
49	st	250				
51	—	3.6				
l	Iobs. 001	Icalc. 001	Iobs. 111	Icalc. 111	Iobs. 221	Icalc. 221
2			—	0.5	vw	0.6
4			vw	4.8	—	5.3
6	vw	21	w	23	vw	24
8	m	110	m	100	w	110
10	m	62	st	280	w	98
12	w	12	vvw	6.3	vw	9.6
14	w	14	w	16	vvw	14
16	st	83	m	79	m+	81
18	vst	440	vst	480	st	450
20	st	170	w	36	w	120
22	m+	100	vw	79	vvw	92
24	w	81	vw	86	vvw	78
26	w	39	w	36	—	39
28	st	280	m	240	w	280
30	w	2.6	—	11	w	1.4
32	w	11	m	20	w	12
34	m	140	m	110	m+	140
36	st	240	m+	240	st	240
38	vvw	19	w	35	—	21
40	st	380	st	280	st	340
42	vvw	11	vw	22		
44	—	3.2	—	4.8		
46	m	240	st	230		
48	w	69	st	46		
50	w+	53	m	110		
52	w+	280				

hkl
0 0 10
1 0 1
1 0 5
1 0 9
1 1 0
0 0 16
1 1 6
1 1 8
0 0 18
1 1 10
1 0 15
0 0 20
1 0 17
2 0 0
1 0 19
1 1 16
2 0 8
{1 1 18, 1 0 21}
2 0 10
{2 1 1, 2 1 3}
{2 1 7, 1 1 20}
{2 0 14, 2 1 9}

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$\approx I_{22l} \approx I_4$
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Table 3

Powder photographs of $BaBi_4Ti_4O_{15}$ Cr K_α radiation.

h k l	10^4 $\sin^2\theta$calc.	10^4 $\sin^2\theta$obs.	*I*obs.	*h k l*	10^4 $\sin^2\theta$calc.	10^4 $\sin^2\theta$obs.	*I*obs.
0 0 10	753	745	w	2 0 16	5443	5440	vw
1 0 1	887	878	m	1 0 25	5582	5581	w
1 0 5	1067	1058	vw	2 1 13	5667	5669	vvw
1 0 9	1489	1481	st	0 0 28	5900	5892	vw
1 1 0	1758	1751	m	2 0 18	5954	5960	m
0 0 16	1927	1915	vvw	{2 1 15	6088	6089	vw
1 1 6	2031	2018	vw	1 1 24}	6093		
1 1 8	2240	2236	vw	1 0 27	6365	6364	m
0 0 18	2438	2423	m^-	2 0 20	6526	6529	vw broad
1 1 10	2511	2504	m^+	{2 2 0	7032		
1 0 15	2572	2567	vvw	2 2 2	7064	7070	w broad
0 0 20	3010	2992	w	2 1 19}	7112		
1 0 17	3054	3051	w	{3 0 5	8099		
2 0 0	3516	3514	m	1 0 31	8111	8104	vvw
1 0 19	3596	3600	w^+	2 2 14}	8114		
1 1 16	3685	3681	w	2 1 23	8376	8365	vw
2 0 8	3998	3996	vw	{2 2 14	8507		
{1 1 18	4196	4186	m	3 0 9	8521	8520	m
1 0 21}	4198			1 1 30}	8531		
2 0 10	4269	4265	w	{3 1 0	8802		
{2 1 1	4403	4402	vw	3 0 11	8812	8802	m
2 1 3}	4418			3 1 2}	8820		
{2 1 7	4764	4774	vw	{1 0 33	9074	9092	w broad
1 1 20}	4768			2 1 25}	9098		
{2 0 14	4991	5009	m^+	{1 1 32	9464	9484	w broad
2 1 9}	5005			2 2 18}	9470		

$00z_2$). Other distributions of Ba should, however, not be excluded; as will be seen the three dimensional Fourier cut along $00z$ (see Fig. 3) seems to favour the following Me arrangement: 4 Bi $\pm 00z_2$ and (2 Ba + 4 Bi) equally distributed over the positions 000 and $\pm 00z_1$.

From Table 1 it is seen that roughly for the same value of l: $I_{00l} \approx I_{20l} \approx I_{22l} \approx I_{40l}$, $I_{11l} \approx I_{31l} \approx I_{33l}$, $I_{10l} \approx I_{21l} \approx I_{30l} \approx I_{32l} \approx I_{41l}$ as might be expected from the above atomic positions with atoms only on the lines $00z$, $\frac{1}{2}\frac{1}{2}z$, $0\frac{1}{2}z$ and $\frac{1}{2}0z$. Table 2 gives calculated and observed intensities for the rows $00l$, $10l$, $11l$, $21l$, $22l$ and $30l$. It was found from the Weissenberg photographs that $0028 \gg 0030$ and $1037 > 1039$ (see Table 2) but the observed ratios do not seem to be as large as those calculated. This is more clearly seen for the rows $40l$ and $30l$ where $4028 < 4030$ and $3037 \geq 3039$. These discrepancies could neither be removed by small variations in the z parameters nor by assuming other distributions of the Ba atoms for the structure factor calculations. Other discrepancies found from Tables 1 and 2 are 222:224, 332:334, 0050:0052 and 1148:1152. However, for most reflexions the agreement is quite good and considering the errors which might be introduced by absorption effects and errors in the ratios f_{Ti}/f_{Bi} and f_0/f_{Bi} the agreement might on the whole be classified as fairly good.

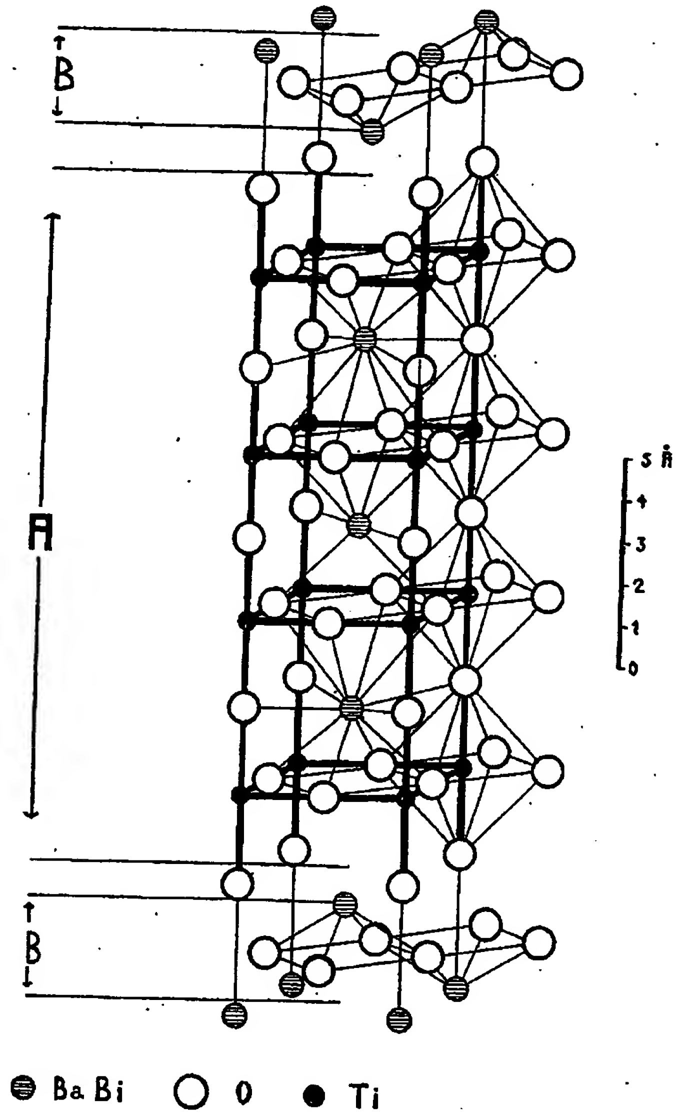

Fig. 4. One half of the unit cell of $BaBi_4Ti_4O_{15}$. A denotes the perowskitic region and B the Me_2O_2 layers.

The following structure is therefore proposed:
$D_{4h}^{17} - I4/mmm$
$(000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2})\ +$

$2\ Me_1$ in 2 (*a*) 000
$2\ O_1$ in 2 (*b*) $00\frac{1}{2}$
$8\ O_2$ in 8 (*g*) $0\frac{1}{2}z;\ 0\frac{1}{2}\bar{z};\ \frac{1}{2}0z;\ \frac{1}{2}0\bar{z}$ $\quad z = 0.048$
$4\ Ti_1$ in 4 (*e*) $00z;\ 00\bar{z}$ $\quad z = 0.452$
$4\ O_3$ in 4 (*e*) $\quad z = 0.402$

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4 Me_2 in 4 (*e*)	$z = 0.106$
8 O_4 in 8 (*g*)	$z = 0.148$
4 Ti_2 in 4 (*e*)	$z = 0.352$
4 O_5 in 4 (*e*)	$z = 0.302$
4 Me_3 in 4 (*e*)	$z = 0.221$
4 O_6 in 4 (*d*) $0\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}0\frac{1}{4}$	

Ba and Bi equally distributed over all Me positions.

If the structure is described by means of an orthorhombic space group (D_{2h}^{23}), as used for the structures of Bi_3NbTiO_9 and $Bi_4Ti_3O_{12}$, the positions will be: $D_{2h}^{23} - F\,mmm$ (000; $\frac{1}{2}\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$) + 4 Me_1 in 4 (*a*) 000, 4 O_1 in 4 (*b*) $00\frac{1}{2}$, 16 O_2 in 16 (*j*) $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\bar{z}$; $\frac{1}{4}\frac{3}{4}z$; $\frac{1}{4}\frac{3}{4}\bar{z}$; $z = 0.048$, 8 Ti_1 in 8 (*i*) $00z$; $00\bar{z}$ $z = 0.452$, 8 O_3 in 8 (*i*) $z = 0.402$, 8 Me_3 in 8 (*i*) $z = 0.106$, 16 O_4 in 16 (*j*) $z = 0.148$, 8 Ti_2 in 8 (*i*) $z = 0.352$, 8 O_5 in 8 (*i*) $z = 0.302$, 8 Me_2 in 8 (*i*) $z = 0.221$, 8 O_6 in 8 (*f*) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

The distances (Å) and coordination will be:

$O_1 - 8\ O_2 = 2.78$	$O_2 - 4\ O_2 = 2.73$	$Me_2 - 4\ O_2 = 3.10$	$Ti_1 - O_3 = 2.09$
$O_3 - 4\ O_2 = 2.84$	$O_4 - 4\ O_4 = 2.73$	$Me_2 - 4\ O_3 = 2.75$	$Ti_1 - 4\ O_2 = 1.93$
$O_3 - 4\ O_4 = 2.84$	$O_6 - 4\ O_6 = 2.73$	$Me_2 - 4\ O_4 = 2.61$	$Ti_1 - O_1 = 2.00$
$O_5 - 4\ O_6 = 2.91$			
	$Me_1 - 8\ O_2 = 2.78$	$Me_3 - 4\ O_6 = 2.28$	$Ti_2 - O_3 = 2.09$
	$Me_1 - 4\ O_1 = 2.73$	$Me_3 - 4\ O_5 = 2.89$	$Ti_2 - 4\ O_4 = 1.93$
		($Me_3 - 4\ O_4 = 3.64$)	$Ti_2 - O_5 = 2.09$

One half of the unit cell is shown in Fig. 4.

I wish to thank Professor L. G. SILLÉN for valuable discussions on this work.

Stockholms Högskola, Institute of Inorganic and Physical Chemistry. May 1950.

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